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INVESTIGATIONS ON LIGHT AND HEAT, PUBLISHED WITH AN APPROPRIATION FROM THE RUMFORD FUND.

II.

CONTRIBUTION FROM THE PHYSICAL LABORATORY OF HARVARD COLLEGE.

ON THE SPECTRUM OF ARSENIC.

BY OLIVER W. HUNTINGTON.

Presented by Professor Trowbridge, June 28, 1881.

IT has been noticed in the case of the spectrum of nitrogen gas, that the spectrum obtained from an electric discharge of low intensity through a rarified atmosphere differs from that obtained when the intensity of the discharge has been increased by a Leyden jar. In the case of the low tension discharge, the bands of the spectrum appear fluted on the more refrangible side; but upon the introduction of a Leyden jar into the circuit the fluted appearance at once vanishes, and the spectrum breaks up into isolated bands. This difference has been ascribed to a difference of condensation of the molecule. Now as arsenic is allied to nitrogen, it was thought the same difference might appear in the spectrum of arsenic, and we proposed to make this a subject of investigation. For this purpose, we first prepared two tubes, — one an ordinary Geisler tube, such as is used for showing the spectrum with rarefied gas; the other as shown in Fig. 1 of accompanying plate, for the spark spectrum with Leyden jar. A small amount of pure metallic arsenic was introduced into each tube, and they were then repeatedly exhausted, each time replacing with hydrogen. After the final exhaustion, the tubes were heated, in order to fill them with the vapor of arsenic. But, upon passing the spark through them, we could obtain no definite or satisfactory result. The arsenic spectrum was feeble, the hydrogen brilliant, and the fluted indefinite bands which accompany the hydrogen spectrum wholly obscured the phenomenon.

Judging from the statements in Roscoe's spectrum analysis that these fluted portions of the hydrogen spectrum were accidental and due to impurities, we attempted to get rid of them in order to bring out the arsenic spectrum. We, therefore, prepared several tubes with pure hydrogen. We arranged tubes with two outlets, in order to pass a continuous current through the whole apparatus, including the Sprengel pump which was connected with one of the openings. The hydrogen was prepared from pure zinc and sulphuric acid, and most carefully dried. We would allow the gas to slowly pass through the apparatus for twenty-four hours, then exhaust, and after exhaustion heat the tube as hot as practicable under the circumstances, then pass dry hydrogen and repeat the process several times. Notwithstanding these precautions, we found, after a great many trials with different tubes, that the fluted and more or less diffused spectrum always accompanied the four principal hydrogen lines. It being then impossible to eliminate the diffused spectrum, we next tried alloying the platinum electrodes with arsenic, and experimented with these in a rarefied atmosphere of hydrogen, both with continuous discharge of Rumkorff coil, and with interrupted discharge with Leyden jar. We now obtained very definite arsenic bands, apparently the same in both cases; but the effect was very momentary, and gave no opportunity for measurement. The spectrum while it lasted was very striking; but, as soon as the arsenic upon the extreme point of the electrode passed off, the characteristic spectrum disappeared.

We were by this experience led to contrive the following apparatus, by which we obtained the desired result, and the same may be useful in experiments on the spectra of similar volatile substances. A longitudinal section of the tube, one half the original size, is shown in Fig. 2 of plate. The portions *AA′* and *A″* are of rather coarse thermometer tubing. *BB′* is a tube left open at *B*, and drawn to a capillary point at *B′*. The substance to be examined, after being reduced to a powder, is introduced through the opening at *B* until the tube is about half full. Then one end of a platinum wire is buried in the substance, and the other end is fused into the tube at *B*, thus closing the opening. After the hydrogen has been allowed to flow through the tube a sufficient length of time, the opening at *A* is closed by a nipper-tap, and the tube is exhausted at *A″*. Now upon connecting *B* with the negative electrode, and *C* with the positive electrode, of a small induction coil, we have the vapor of the substance in the tube *BB′* carried in the current through the tube *A′* where the spectrum may be observed.

One advantage of this particular form of tube is, that, in order to compare the spectrum of our substance with that of hydrogen, we have only to reverse the current, making *C* the negative pole, and then all the lines except those of hydrogen at once disappear.

The arsenic spectrum thus obtained is very brilliant, and consists of

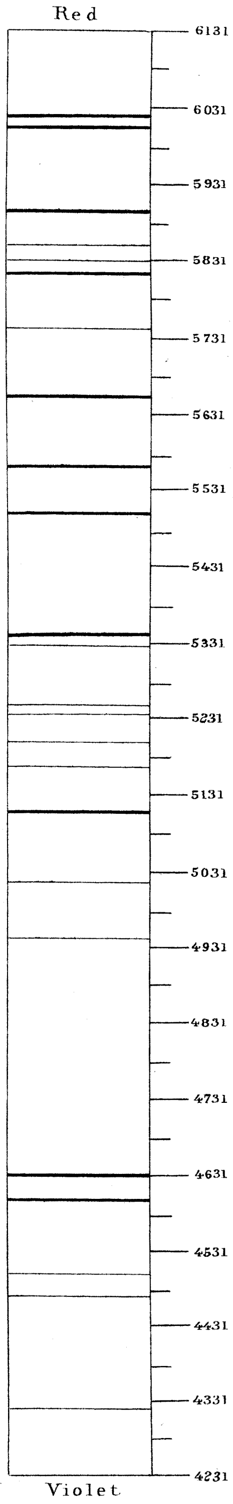

Fig. 3.

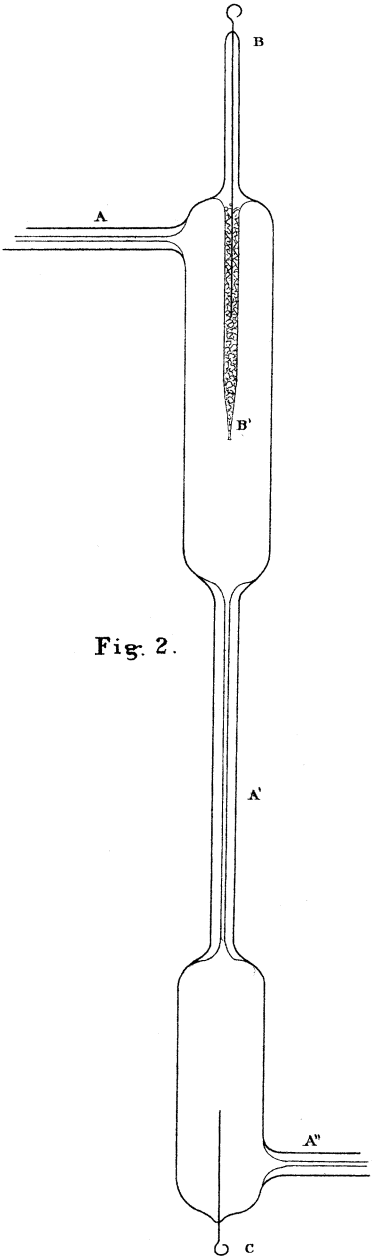

Fig. 2.

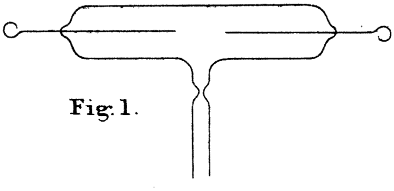

Fig. 1.

numerous well-marked sharply defined bands. The bands are most numerous and brilliant in the green, and these give the prevailing tone to the spectrum. But there is one very striking yellow band, and there are also several bands in the blue and violet. Then in the red there is an interesting double band, the two members of which are the same distance apart as the two *D* lines. In addition, there may be also a more or less diffused spectrum, which in some parts cannot be distinguished from the similar diffused spectrum of hydrogen, and it is worthy of remark in this connection, as indicating the purity of the material used, and also that the diffused fluted spectrum above referred to cannot come from the material of the tube, that no trace of the sodium line was seen. No account was taken of the diffused spectrum, as it only appeared when the battery was unusually strong.

In speaking of the diffused spectrum of arsenic, we do not mean the same kind of diffused spectrum as mentioned above in connection with nitrogen. The diffused arsenic spectrum appears to be composed of innumerable faint lines, wholly independent of the other more brilliant characteristic arsenic bands; and we only use the term "diffused" for convenience, to express that the lines are very faint and too numerous to measure.

The arsenic employed had been carefully purified by sublimation, and preserved under distilled water. We used for measuring the wave-lengths of the spectrum lines the spectroscope described by Professor J. P. Cooke [Am. Jour. of Science, Vol. XL., Nov., 1865]. In this instrument, the train of prisms can be adjusted accurately to the angle of minimum deviation, which was observed in each case. We used five flint prisms of 45° angle each, and to reduce the angular measurements to wave-lengths, we employed the method described by W. M. Watt in his "Index of Spectra."

We, in the first place, measured with care the angles of minimum deviation of the most prominent Frauenhoffer lines, and verified and somewhat multiplied the data by measuring also the angles for characteristic lines of the hydrogen, lithium, sodium, thalium, and strontium spectra. These we combined with the wave-lengths of the same lines given by Angström, by ordinates and abscissas in the usual way, and the curve drawn through the points so determined was so regular and of such small curvature, that it was easy to interpolate with minutes of arc to five *tenth-metres* of wave-length, as usually expressed.

The instrument is capable of reading to five seconds of arc, and with the full bank of ten prisms it would give the wave lengths to tenth-metres with perfect accuracy. With the comparatively feeble light of the arsenic spectrum, as we first observed it, we did not think it advisable to use the full power of the instrument. We therefore used five prisms, as stated, and read to one minute of arc. We always began each series of observations by setting the cross-wire of the micrometer on the sodium line, after the telescope had been adjusted to the angle of minimum deviation of this line as first observed. There was seldom any observed difference in this angle. But when by change of temperature, or otherwise, an alteration of two or three minutes had taken place, we found, on readjusting the cross-wire, that the relative position of the spectrum lines was, to the limit of accuracy of our measurement, wholly unchanged.

We give below the table of wave-lengths of the principal lines of the arsenic spectrum.

6023 tenth-metres.
6013 “
5853 “
5833 “
5813 “
5743 “
5653 “
5563 “
5498 “
[**5340**] “
5323 “
5245 “

5230 tenth-metres.
5195 “
5163 “
5103 “
5013 “
4941 “
4623 “
4593 “
4493 “
4463 “
4313 “

The wave-lengths printed in heavy type denote the bands which are most brilliant and give character to the spectrum. The other lines are less constant and less distinct, and in some instances may be due to accidental causes.

We were surprised to find among the bright lines, that the one which in the table is enclosed in brackets corresponds to the green thalium band, and upon examining the spectrum it appeared evident that thalium must be present in the arsenic in large quantities, as the thalium band was fully as bright as any of the arsenic bands.

The accompanying diagram (Fig. 3 of plate) will give some idea of the general appearance of the arsenic spectrum.